

Local Electrical Properties of Polyaniline-ZnO Nanocomposite Langmuir-Blodgett Thin Films Investigated Using Conductive Atomic Force Microscopy

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Abstract

The localized electrical properties of Langmuir-Blodgett (LB) thin films of polyaniline (PANi) dispersed with Zinc oxide (ZnO) nanoparticles were investigated using Conductive Atomic Force Microscopy (CAFM). The nanoscale electrical conductivity of PANi-ZnO nanocomposites was analyzed by mapping current distribution and evaluating single-point current-voltage (I-V) characteristics. The CAFM results indicate a uniform charge transport network, reduced defect density, and enhanced conductivity in ZnO-incorporated films. The CAFM current mapping revealed a uniform distribution of conductive domains across the film surfaces, showing homogeneity of nanocomposite thin films. These insights contribute to the understanding of the electrical behavior of PANi-based nanocomposites, which holds promising potential for applications in electronic devices.

Keywords: Conductive AFM, Polyaniline-ZnO, Nanocomposite, Langmuir-Blodgett Film, Nanoscale Conductivity

Introduction

Polyaniline (PANi), a conducting polymer, has been widely explored for its potential in flexible electronics and optoelectronics. However, its conductivity and stability can be significantly improved by incorporating inorganic nanomaterials such as Zinc oxide (ZnO). ZnO nanoparticles offer high charge

mobility and excellent optoelectronic properties, making PANi-ZnO nanocomposites suitable for next-generation electronic applications. Langmuir-Blodgett (LB) thin film deposition is an effective technique for controlling the nanostructured arrangement of organic-inorganic materials and fabricating ultrathin films with controlled

morphology and organization [1-4]. The combination of LB deposition and Conductive Atomic Force Microscopy (CAFM) enables a detailed investigation of the electrical properties of these nanocomposites at the nanoscale. In particular, Conductive Atomic Force Microscopy (CAFM) has emerged as an effective tool for probing the local electrical properties of thin films at a very high resolution. By mapping current variations across the surface of nanocomposite films, CAFM enables a detailed analysis of the film's electrical homogeneity, defect density, and overall conductivity [5].

This study presents a novel nanoscale investigation of Polyaniline-ZnO Langmuir-Blodgett (LB) thin films using Conductive Atomic Force Microscopy (CAFM), providing insights into their localized electrical properties focussing on the current distribution, conductivity variation, and current vs voltage (I-V) characteristics of PANi-ZnO LB films.

Experimental Details

Materials and Preparation of PANi-ZnO LB Films

Materials: Polyaniline (PANi) was synthesized via oxidative polymerization of aniline (LR for synthesis, purity 99%, from

Loba chemie Ltd.), while zinc oxide (ZnO) nanopowder (<50 nm, purity 97%) from Sigma-Aldrich with molecular weight 81.39g/mol.

Film Composition: Different weight percentages of ZnO in PANi were prepared as reported earlier [5, 6] (5 wt%, 10 wt%, 15 wt%, and 20 wt%) for electrical analysis.

Langmuir-Blodgett Film Formation: The LB (using KSV-NIMA, Espoo, Finland setup) films were fabricated by spreading PANi-ZnO dispersion (in N-Methylpyrrolidone (LR, purity 99.5% from S. D. fine-chemicals, onto a water subphase (Milli-Q filtered (Direct Q 3) deionized and ultrapure water (Resistivity=18.2 MΩ.cm)), followed by compression and deposition onto ITO-coated glass substrates using the LB technique (Bhullar et al., 2015b). The deposition was carried out at room temperature and controlled pressure to ensure uniformity in film formation [6,7].

Conductive Atomic Force Microscopy (CAFM) Characterization

AFM (Solver-NEXT NT-MDT, Zelenograd, Russia) equipped with a Pt-coated conductive probe was used to measure nanoscale electrical properties. CAFM was operated in contact mode, scanning an area of $2 \times 2 \mu\text{m}^2$. Single-

point I-V measurements were performed at marked locations. Conductance spectra (dI/dV vs. V) and normalized conductance $\{(dI/dV)/I/V\}$ were extracted to evaluate the

Results and Discussion

Topographical Analysis of PANi-ZnO Films

The AFM topography images (Figure 1 a-d) of the PANi-ZnO LB films revealed a mountain-valley-like pattern, suggesting nanoscale roughness. The presence of hexagonal ZnO nanoparticles was observed, which formed close-packed structures due to isotropic

electrical behavior. A 3D current distribution image of the PANi-ZnO film was obtained to provide a clearer visualization of the conductive behavior across the surface.

interparticle interactions, as reported in previous studies [6].

At lower ZnO concentrations (5-10 wt%), ZnO nanoparticles are well dispersed within the PANi matrix, whereas higher ZnO content (15-20 wt%) may result in localized aggregation, which can influence charge transport pathways.

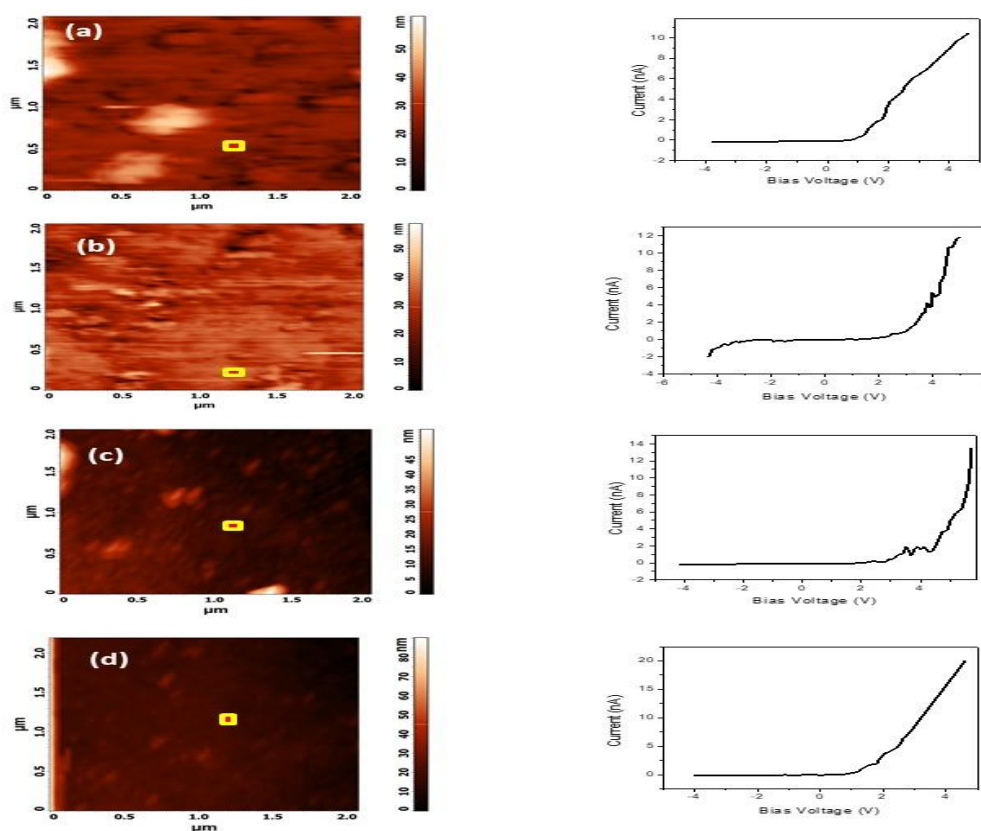


Figure 1. Height profile (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % weight of ZnO in PANi; and Single-point electrical I–V characteristics corresponding to the positions (squares) marked on images (a-d). The I–V characteristics show currents ranging up to 8 nA in 5%, 12 nA in 10%, 14 nA in 15% and 20 nA in 20 wt%

Single-Point I–V Characteristics

The I–V curves (Figure 1) demonstrate a nonlinear current response, characteristic of semiconducting behavior. The steepest slope in high ZnO content films, confirming increased conductivity. The presence of charge injection barriers, which decrease as ZnO concentration increases. The measured maximum current values are 8 nA for 5 wt%

ZnO, 12 nA for 10 wt% ZnO, 14 nA for 15 wt% ZnO, and 20 nA for 20 wt% ZnO.

Conductance and Normalized Conductance Spectra Analysis

Fig 2(a) shows the conductance (dI/dV) spectra for PANi, PANi–ZnO (10 wt %) nano-composite LB films showing an increasing conductance with ZnO content, particularly above 2V bias.

Fig 2(b) show Normalized conductance $\{(dI/dV)/(I/V)\}$ spectra derived from I–V data revealing that PANi–ZnO film displays relatively stable conductance behaviour across a wide voltage range, suggesting that the ZnO nanoparticles aid in charge transport by reducing fluctuations in conductivity.

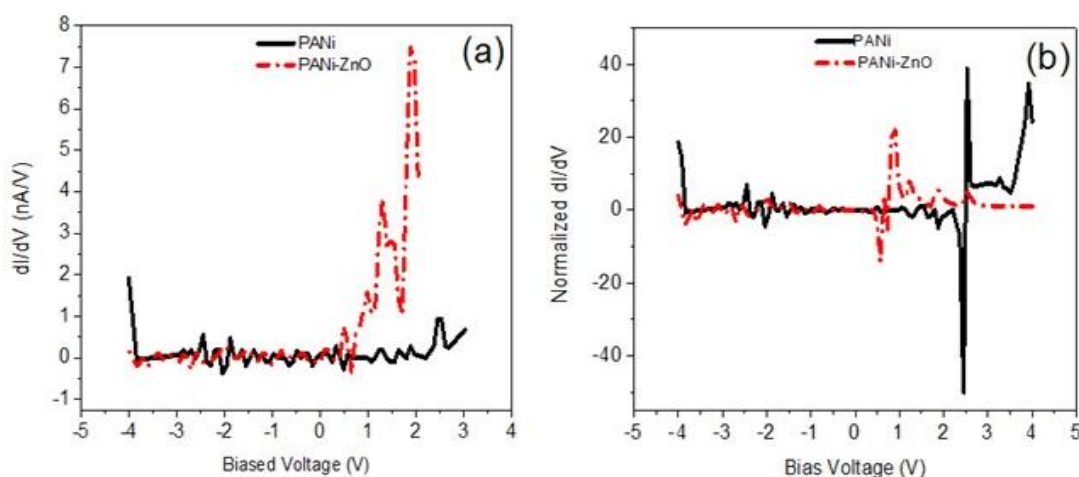
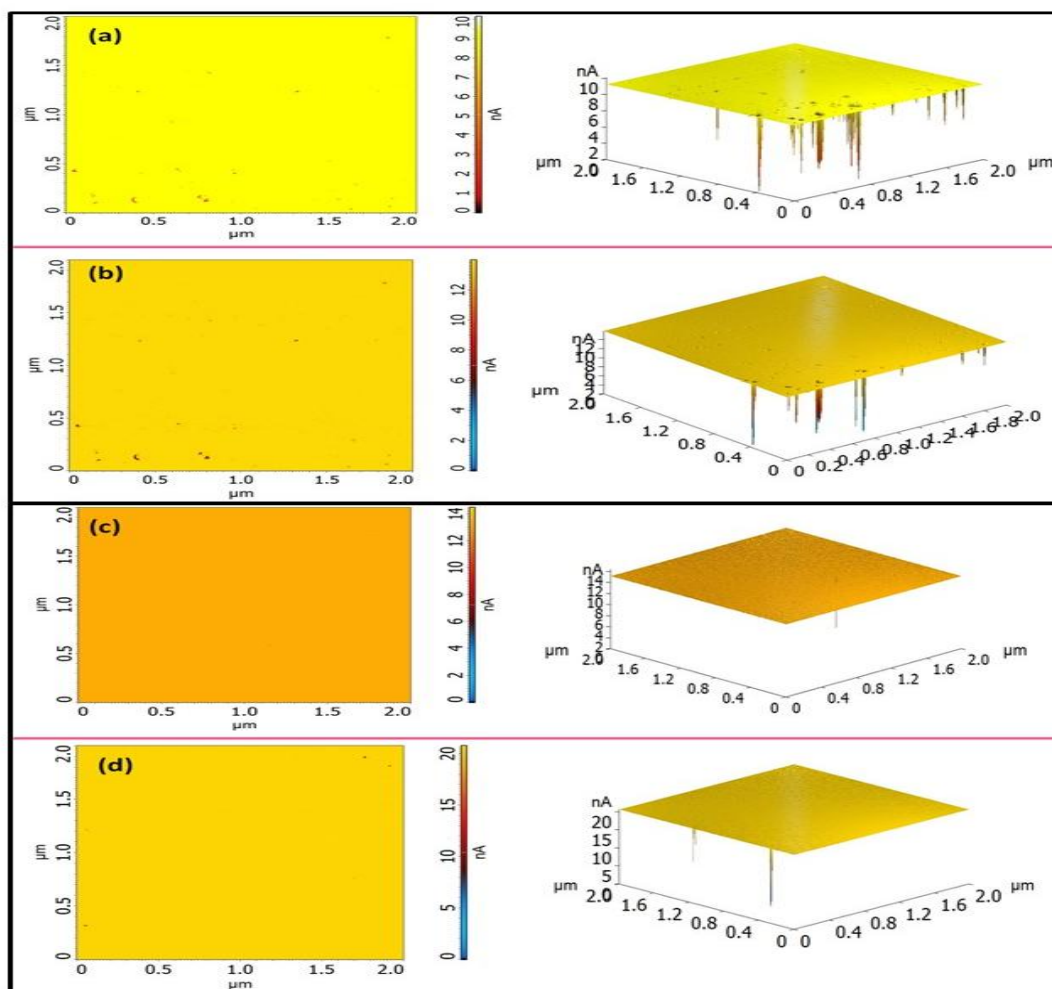


Fig 2(a) Conductance (dI/dV) spectra for PANi, PANi-ZnO (10 wt %) nano-composite LB film and (b) Normalized conductance $\{(dI/dV)/(I/V)\}$ spectra derived from I-V data.

Current Mapping by CAFM

Figure 3 (a-d) presents CAFM current maps in Contact mode, of (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % PANi-ZnO nano-

composite LB films and their corresponding 3D images. The current distribution is relatively uniform, confirming efficient charge percolation across the films. The homogeneity suggests strong interfacial interactions between PANi and ZnO, reducing percolation pathways for charge transport [5,6].



Conductive data images in Contact mode, scan range $2 \times 2 \mu\text{m}^2$ (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % PANi–ZnO nano-composite LB films and their corresponding 3D images.

Higher ZnO concentrations contribute to enhanced charge transport due to strong π - π interactions between PANi and ZnO, which facilitate electron delocalization. The 3D surface plot shows a highly uniform distribution of current-conducting pathways, with minimal fluctuations in current intensity. The current is consistently spread across the surface with only minor localized variations. This suggests that the ZnO nanoparticles are uniformly integrated into the PANi matrix, enhancing the overall electrical conductivity and reducing the formation of conductive "hot spots."

A very few localized disruptions in the current distribution displayed in the 3D image of the zPANi-ZnO films may arise from aggregation of ZnO nanoparticles and weaker interfacial interactions between the nanoparticles and the polymer, leading to less efficient electron transport. The uniform and smooth current distribution observed in the PANi-ZnO films correlates with better charge transfer efficiency and suggests that ZnO enhances the overall electrical properties of the PANi composite.

The improved dispersion of nanoparticles in PANi-ZnO films leads to a more homogeneous conductivity, making them more suitable for applications in electronic devices.

Interpretation and Mechanism

The enhanced electrical properties observed in PANi-ZnO Langmuir-Blodgett (LB) films can be attributed to several key factors. First, interfacial charge transfer is promoted by the ZnO nanoparticles, which facilitate charge hopping between PANi chains, thus minimizing defect-related charge traps. Second, π - π stacking interactions between the PANi chains are enhanced, leading to improved alignment of the conjugated chains and, consequently, better carrier mobility. Finally, percolation pathways are formed by the ZnO nanoparticles, acting as conduction bridges that create efficient networks for charge transport, further enhancing the conductivity of the nanocomposite films.

Conclusion

The CAFM investigation of PANi-ZnO LB thin films revealed a uniform current distribution, lower defect density, and enhanced charge transport properties. This work correlates nanoscale charge transport with film morphology, revealing uniform current distribution, reduced defect density,

and enhanced conductivity due to strong ZnO-PANi interfacial interactions. The findings suggest potential applications in nanoelectronics, sensors and flexible devices, bridging the gap between structural characterization and electrical performance optimization in conducting polymer nanocomposites.

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